THE EFFECTS OF THE NOVEMBER 1981 LIQUID-FERTILIZER PIPELINE BREAK ON GROUNDWATER IN PHELPS COUNTY, MISSOURI

By
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Author's Note….

In November 1981, just over a quarter century ago, a leak from a fertilizer pipeline near the Phelps-Dent County line severely affected the quality of water discharging from Maramec Spring nearly 13 miles northeast of the site of the spill. In the weeks that followed the spill, several county, state, and federal agencies as well as private entities gathered information to assess the impacts to groundwater, surface water, aquatic wildlife, and human health. More was learned about the Maramec Spring flow system during this few week period than was previously known. The effects of the spill on Maramec Spring's water quality could be detected for only about 7 weeks. During that period, dissolved oxygen levels rapidly decreased from normal to levels so low that fish, crayfish, and other aquatic animals could not survive, resulting in loss of aquatic life. Nearly seven weeks later, water quality at Maramec Spring recovered to pre-spill conditions.

The following technical report was originally prepared in early 1982 to document the effects of the spill, to present the hydrologic data gathered during the event, and to illustrate how the Maramec Spring karst drainage system functions. For a variety of reasons, the report was never formally published as a Water Resources Report or an Open File Report. Dozens of copies have been made over the past 25 years and provided to anyone desiring to learn about the spill and the Maramec Spring flow system, but the report has never been made easily available. Other than a few editorial changes and the addition of several photographs, the report has not been significantly altered from the version produced in 1982. The report was finished before a water trace was conducted to definitively establish the hydrologic connection between the spill site and Maramec Spring. An addendum has been added to the end of the report to discuss the water trace results.

Although the effects of the spill have long since dissipated, the hydrogeologic knowledge gained in the weeks following the release is still of great value. Pipelines cross all parts of Missouri and carry a variety of substances from fertilizers to petroleum products. Some transect areas where a spill would only impact groundwater in the immediate vicinity of the release. Other pipelines pass through the Springfield and Salem plateaus of the Ozarks, where spills in karst recharge settings could impact springs many miles distant. In some ways, Maramec Spring was fortunate in that the spilled material was a water-soluble contaminant. It caused severe, but brief, water-quality problems. A few rainfall/recharge events flushed the contaminants through the groundwater system. The effects of a spill from a petroleum pipeline in a similar setting would have been much different and of a much longer duration.

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August, 2007
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ABSTRACT

In November 1981, a leak from a buried section of an ammonium nitrate-urea pipeline released a large amount of nitrogen-rich material in a karst watershed in south central Missouri. The spill occurred adjacent to Dry Fork, a losing stream, which recharges Maramec Spring. Low dissolved oxygen conditions severely damaged the trout population at the spring and several species of cave fauna that live in the spring system.

Water-quality degradation began at the spring eight days after the spill was reported. Dissolved oxygen decreased from the normal 7 to 9 mg/L to less than 0.2 mg/L. Nitrite plus nitrate content peaked at 4.2 mg/L and ammonia levels exceeded 2 mg/L. The pipeline company initially estimated that the spill released only about 1,344 gallons (5,087 L). However, calculations based on water-quality samples and daily discharge measurements at Maramec Spring indicate that about 24,100 gallons (9.14×10^4 L) of liquid fertilizer leaked from the pipeline. A hydrograph analysis of Maramec Spring and water-quality samples indicate that the leak probably began at least five days before it was discovered.

Water samples taken from about 381 private wells in middle and lower Dry Fork watershed and adjacent areas indicated that the pipeline break did not affect private wells in the area. Seventeen wells were found to contain greater than 10 mg/L nitrate. More detailed chemical analysis of samples from these wells indicate that they were being contaminated by a source other than the pipeline, probably from septic systems or livestock waste.

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Introduction

Dry Fork, a tributary of the Meramec River, heads in north-central Dent County and flows through southeastern Phelps County, Missouri. The watershed has a surface area of approximately 380 mi² (984 km²). Dry Fork flows into the Meramec River about 1 mi (1.6 km) downstream from Maramec Spring (figure 1).

The area is underlain predominantly by Lower Ordovician cherty dolomite and sandstone. The Gasconade Dolomite, oldest unit exposed in the basin, crops out along lower valley walls and forms the stream bed for Dry Fork in many locations. The overlying Roubidoux Formation consists of interbedded sandstone and dolomite with abundant chert, and forms the bedrock surface over most of the basin. This unit reaches a maximum thickness of about 150 feet (46 m) but is typically somewhat thinner, due to solution removal of the carbonate interbeds. The Jefferson City Dolomite, a finely crystalline argillaceous dolomite unit, crops out along the northern and western watershed divide. Bedrock in most of the basin is overlain by residuum consisting of clay and chert fragments and sand, the insoluble remainder of the host rocks. Residuum thickness, locally exceeding 100 feet (30 ml) in the southern part of the basin and thinning northward, reflects the deep weathering in the area.

All of the carbonate units in the basin have been solution altered to some degree. Karst features are abundant in the area. The southern part of the basin contains many sinkholes, ranging up to about 100 feet (30 m) deep and 1,000 feet (300 m) in diameter, but they are not common in the central and northern parts of the watershed. The basin contains several caves in dolomite interbeds of the Roubidoux Formation and in the Gasconade Dolomite. Large springs are absent. Maramec Spring, just outside of Dry Fork basin, is apparently recharged from Dry Fork basin (Vineyard and Feder, 1974). Only a few small springs occur along Dry Fork or its major tributaries. The most abundant karst features in the basin are losing streams, those that contribute almost all their flow to the groundwater system. Significant reaches of middle and upper Dry Fork and most of Norman Creek, a major tributary, are losing streams. Karstification of the area has resulted not only in surface karst features but also has greatly affected the groundwater system. A well-developed conduit system, formed by subsurface removal of carbonate rock, drains portions of Dry Fork basin. The well-integrated network of subsurface drainage causes much of Dry Fork and most of its major tributaries to by typically dry except during extended periods of precipitation or after major storms.

Average annual rainfall for the area is about 39 inches per year (990 mm/yr). Rainfall-runoff characteristics and groundwater-level data from wells in Dry Fork basin indicate much of the precipitation falling on middle and upper parts of the basin rapidly enters the subsurface. Hydrographs of Maramec Spring show rapid response in spring discharge after precipitation in Dry Fork basin. Spring discharge begins increasing a few hours after precipitation begins and, after brief periods of moderately intense precipitation, peaks within 24 hours, a response due to

pressure-head increase in the area of precipitation. Water flowing from Maramec Spring for the first few days after a major rainfall is water that had already been in transit. Water from precipitation reaches the spring sometime after the hydrograph peak, the time lapse depending on rainfall location, pre-rainfall spring stage, and other geologic and hydrologic factors.

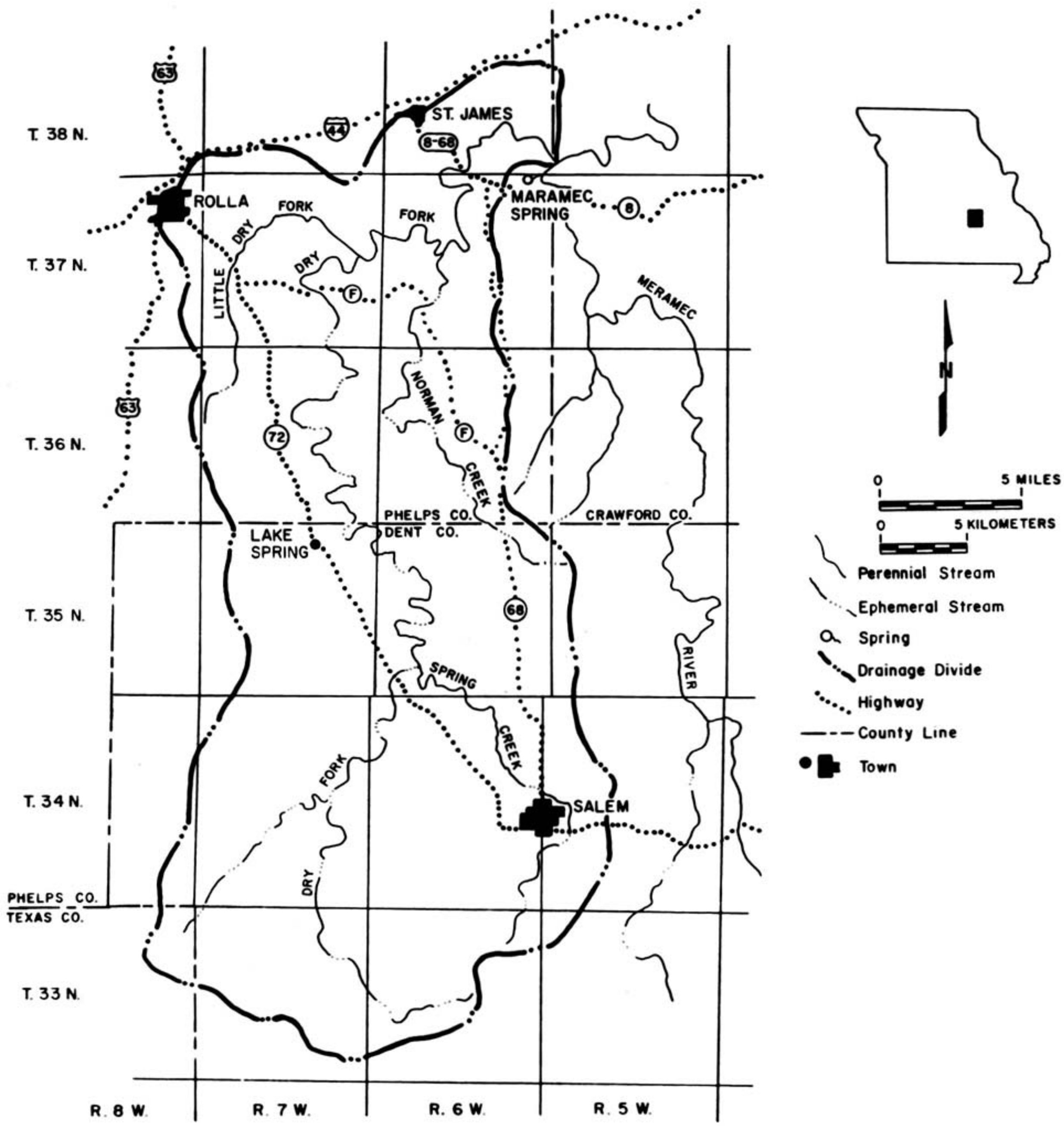

Figure 1: Location map of the Dry Fork basin-Maramec Spring area.

Low-flow measurements of Dry Fork at Highway 8-68 indicate that the stream is deficient in groundwater inflow. Calculated 7-day Q_2 and 7-day Q_{10} flows are 1.2 ft^3/sec (0.034 m^3/sec) and 0.3 ft^3/sec (0.008m^3/sec), respectively. In contrast, the Jacks Fork River at Eminence, Missouri, with a drainage area of 398 mi^2 (1,030 km^2), has 7-day Q_2 and 7-day Q_{10} flows of 130 ft^3/sec (3.68 m^3/sec) and 80 ft^3/sec (2.26 m^3/sec), respectively, the result of appreciable groundwater inflow. The North Fork River at Twin Bridges, Missouri also has a drainage area similar to Dry Fork but much higher mean annual flow. The 7-day Q_2 and 7-day Q_{10} flows for this river are 38 ft^3/sec (1.08 m^3/sec) and 26 ft^3/sec (0.74 m^3/sec), respectively. Work by Gann and Harvey (1975) shows both Dry Fork and Norman Creek lose significant quantities of water to the groundwater system. Figure 2 shows seepage-run data for Dry Fork basin. During drier portions of the year, there is no flow in Dry Fork from about 4 miles (6.4 km) below Spring Creek to approximately Highway F, about 12 miles (19.3 km) downstream (photo 1). After moderate precipitation, Dry Fork will flow in the headwaters area; nevertheless, flow generally ceases a few miles downstream from Spring Creek. Only after heavy rainfall is there flow in lower Norman Creek and some portions of Dry Fork.

Photo 1. Dry Fork below Spring Hill Road (Sec. 11, T. 36 N., R. 7 W.)

Maramec Spring is thought to be the discharge point of much of the water lost in middle and upper Dry Fork basin and Norman Creek. Maramec Spring rises in a circular basin at the base of the bluff of Gasconade Dolomite. The phreatic cave, explored by divers to a depth of 195 ft (59 m) and to a distance of over 1,700 ft (518m), at the bottom of the 17 ft (5.2 m)-deep spring pool, channels water to the spring opening. With an average discharge of 144 ft^3/sec (4.07 m^3/sec), the spring is the third largest in Missouri.

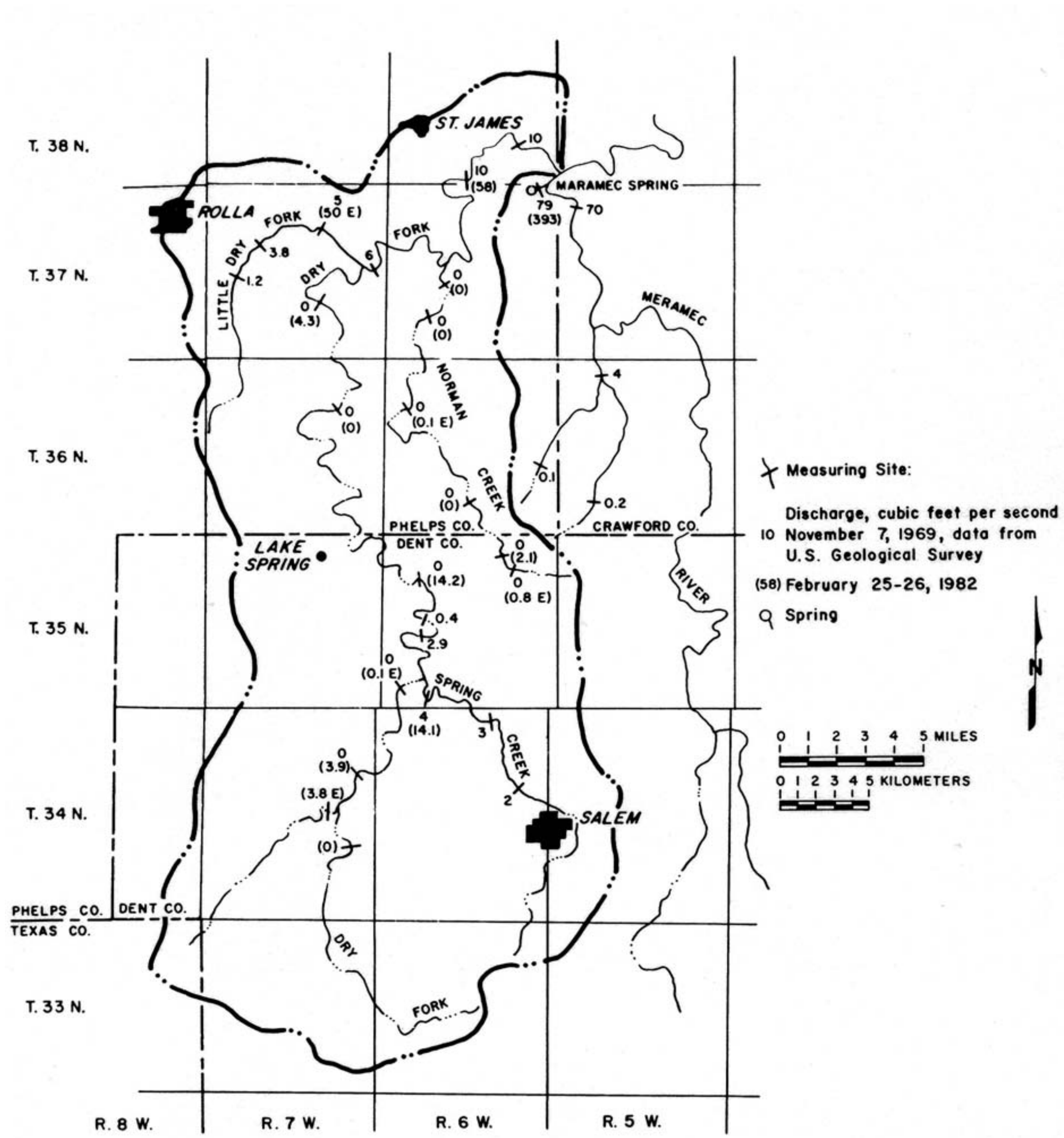

Figure 2: Seepage-run data showing several areas of surface-water loss in Dry Fork basin.

On November 15, 1981, a buried section of pipeline owned by Williams Pipeline Company was reported to be leaking where the line crosses an unnamed spring-fed tributary of Dry Fork in Sec. 35, T. 36 N., R. 7 W. (photo 2, figure 3). The pipeline was carrying liquid nitrogen fertilizer (45.1 percent ammonium nitrate, 34.8 percent urea, 20.1 percent water). Spilled material that surfaced followed the unnamed tributary approximately 1,100 ft (335 m) to Dry Fork, which was not flowing at this time upstream from the spill. Downstream for about 1 mile (1.6 km), the creek contained a series of large pools, with flow occurring between them (photo 3). At the terminus of the pools, the creek bed again became dry. Downstream there were scattered pools, but no flow, for approximately 9.5 miles (15.3 km).

Photo 2. Spill site after pipeline had been repaired.

Photo 3. Pools of high-nitrogen water in Dry Fork downstream of the spill site.

When notified, Environmental Emergency Response personnel from the Missouri Division of Environmental Quality visited the spill site. The break was being repaired at the time, and the spill volume initially estimated by Williams Pipeline Company indicated the leak to be minor; only about 32 barrels, or 1,344 gallons (5,087 L), had been lost. For clarity, a time sequence accompanies calendar dates in this report, Day 0 being November 15, 1981, the date the spill was reported.

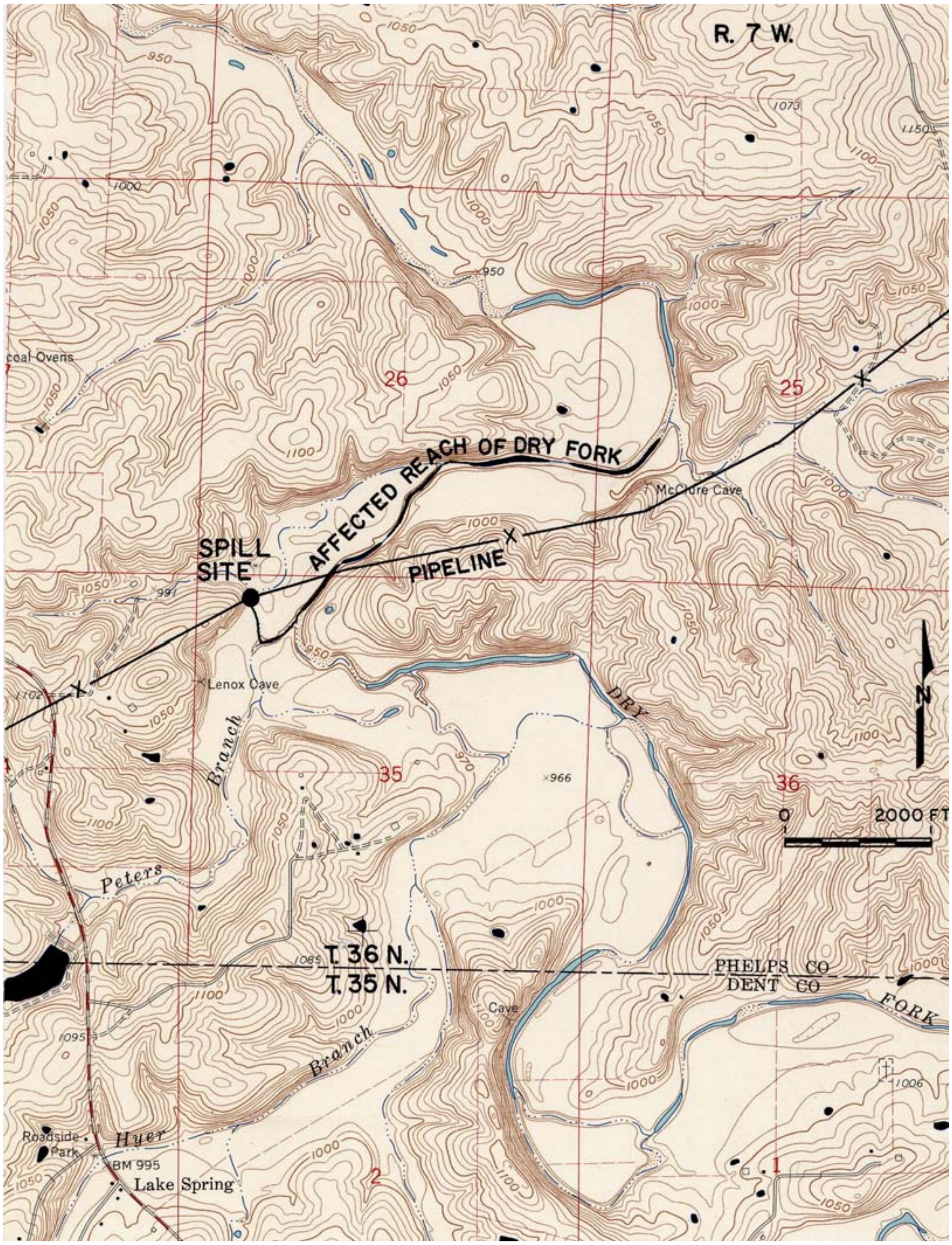

Figure 3: Map showing the location of the November, 1981 pipeline break near Dry Fork. Base map from the Lecoma 7½' quadrangle.

On Day 5 (November 20) dissolved oxygen content at Maramec Spring measured essentially normal at 7.0 mg/L. On Day 7 (November 22), Rainbow trout in concrete impoundments fed by Maramec Spring began showing signs of stress associated with low levels of dissolved oxygen. On Day 8 (November 23), however, it measured 3.0 mg/L; on Day 9 (November 24), 1.0 mg/L. Dissolved oxygen content decreased to a minimum of less than 0.2 mg/L and remained below 1.0 mg/L for 8 days. An enormous effort was needed to keep the fish alive. Numerous large pumps aerated the spring water, increasing the oxygen content in the concrete impoundments to survival levels. About 37,000 sculpins and large spring-basin trout that could not be caught and released downstream were killed (photo 4). Three species of cave fauna living in the cave system were severely affected: *Cambarus hubrichti* (cave crayfish), *Typhlichthys subtrerraneus* (southern cavefish), and *Typhlotriton speleaus* (Ozark blind cave salamander). The Department of Conservation estimates that over a thousand cavefish were lost downstream. By the time oxygen levels increased to a point where aquatic life could survive, spring-basin animals that had not been removed were dead. Dissolved oxygen began to increase on Day 17 (December 2) and generally increased daily for the next 10 days. On Day 27 (December 12) levels began decreasing again, from 6.7 mg/L to 4.7 mg/L on Day 30 (December 15). On Day 31 oxygen content began increasing again, and after Day 44 (December 29) it was essentially normal (figure 4).

Beginning on Day 8 (November 23), Department of Conservation personnel regularly collected water samples from the spring. Samples were preserved with sulfuric acid, cooled, and shipped to the Division of Environmental Quality Laboratory in Jefferson City, Missouri for nitrogen analysis.

Based on published water quality data, nitrate concentration from Maramec Spring ranges from 0.34 to 0.81 mg/L, and averages about 0.56 mg/L. Average background ammonia and nitrite values are considered to be about 0.02 mg/L and less than 0.05 mg/L, respectively. Total nitrogen is estimated to average 0.63 mg/L. Nitrite + Nitrate (NO_2 + NO_3) content of Maramec Spring on Day 8 (November 23) was 3.5 mg/L. Nitrogen content peaked about Day 12 (November 27), with ammonia (NH_3) at 2.0 mg/L and nitrite + nitrate at 4.2 mg/L. Ammonia levels dropped rapidly to less than 0.2 mg/L by Day 17 (December 2). Nitrite + nitrate content also continued to decrease. By Day 25 (December 10), NO_2 + NO_3 content had dropped to 1.4 mg/L, but on Day 27 (December 12), it began to rise again, peaking at 2.5 mg/L on Day 30 (December 15). After Day 30 (December 15) nitrogen levels dropped steadily and measured about 1.0 mg/L on Day 47 (January 1) (figure 4). Nitrogen levels remained at approximately 1.0 mg/L from Day 47 (January 1) to Day 93 (February 16), indicating that pre-spill background nitrogen content may have been higher than historical values. Specific conductance measurements taken at the spring throughout the period of low dissolved oxygen correlate well with dissolved oxygen readings and nitrogen values. Conductance increased from 275 micromhos/cm (µmhos/cm) on Day 8 (November 23) to 320 µmhos/cm on Day 14 (November 29). Conductance decreased from Day 15 (November 30) to Day 26 (December 11), when it measured 280 µmhos/cm (figure 4).

Photo 4. Dead trout at Maramec Spring.

Estimation of the Amount of Fertilizer Spilled from the Pipeline

Shortly after the water quality problem began at Maramec Spring, it became apparent that the initial spill estimate was too low. Discharge data and water quality samples from Maramec Spring, however, allow calculation of the minimum amount of fertilizer spilled.

Discharge measurements are taken daily at Maramec Spring. At approximately 7:00 a.m. each day, Department of Conservation personnel read stage values from a U.S. Geological Survey staff gage on the spring branch; a stage-discharge rating table prepared by the USGS is used to convert stage readings to discharge values. Beginning on Day 8 (November 23), water samples were collected regularly at the spring at about 8:30 a.m. Average daily discharge of the spring was calculated using a bar-graph plot of discharge derived from the spring hydrograph. Each day was assumed to begin and end at 8:00 p.m. For example, the discharge value used for November 29 reflects the portion of the hydrograph record between 8:00 p.m., November 28 and 8:00 p.m., November 29. This was done to center discharge and water quality data more closely in the 24-hour increments being analyzed. Nitrogen values, the sum of ammonia, nitrite, and nitrate, were plotted in a similar way; the average daily values were determined graphically. Estimating background nitrogen for Maramec Spring is difficult. Historical data suggest the value to average about 0.63 mg/L. However, three months after the spill, nitrogen values were still slightly above 1 mg/L. Maramec Spring nitrogen content on Day 47 (January 1) measured 1.0 mg/L and remained essentially constant, ranging from 0.93 mg/L to 1.38 mg/L through Day

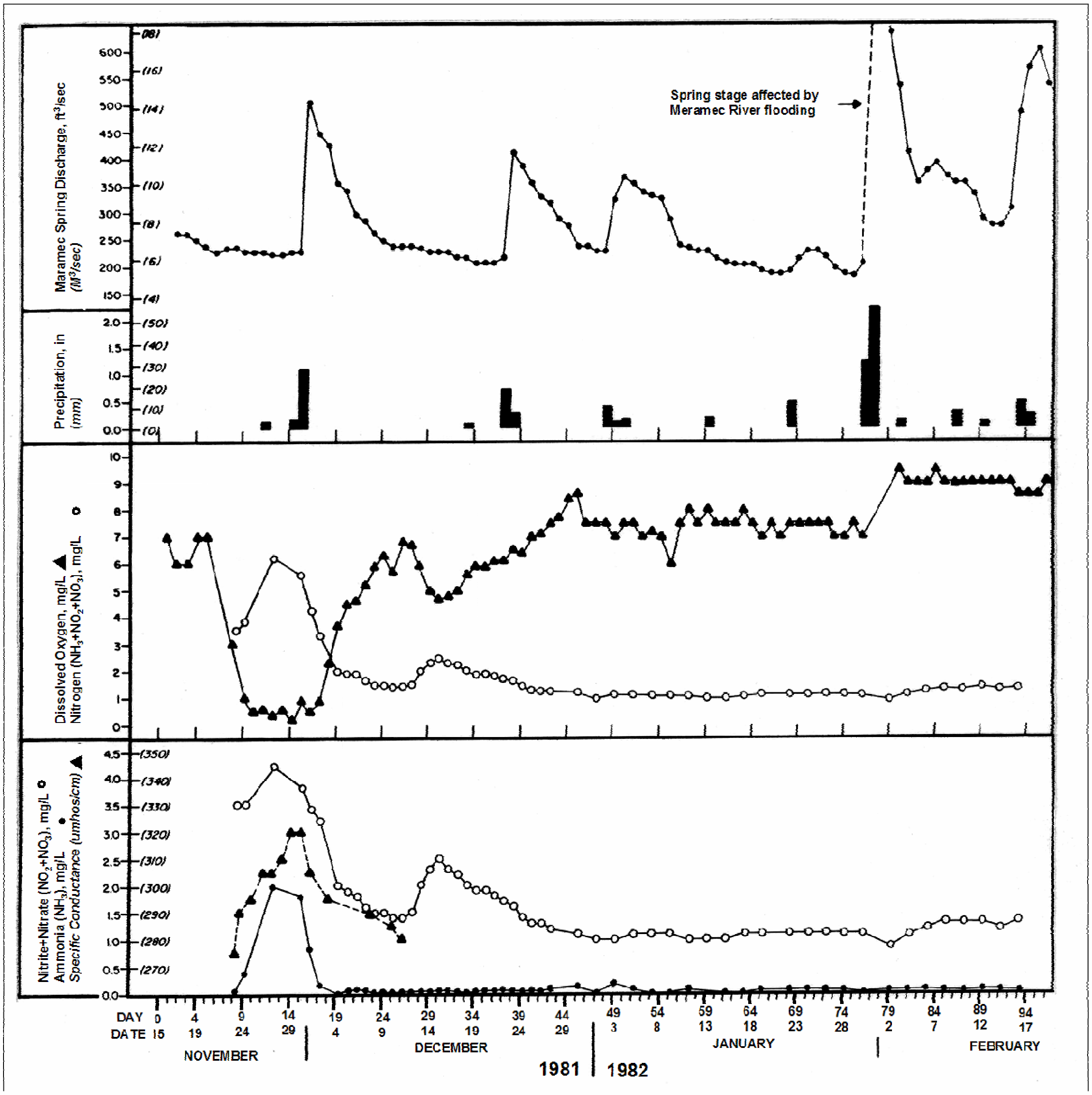

Figure 4: Water-quality and flow data for Maramec Spring. Precipitation shown as weighted averages from four National Weather Service recording stations (Rolla Univ. of MO, Cook Stations, Salem and Licking 4N). Weighted precipitation values less than 0.1 inches not shown.

94 (February 17). Considering the amount of precipitation and recharge during this period, it seems doubtful that after this length of time the spill was still affecting Maramec Spring. Historical nitrogen data from Maramec Spring typically reflect water quality during low-flow periods, when discharge was generally below 100 ft^3/sec (2.83 m^3/sec). Maramec Spring's discharge from Day 8 (November 23) to Day 94 (February 17) averaged 288 ft^3/sec (8.16 m^3/sec), more than twice the long-term average discharge. In karst areas, rapid runoff from

storms introduces lower quality water into spring systems, which could easily increase nitrogen content. Runoff and groundwater recharge is relatively high during winter months, due to lack of vegetation and low evapotranspiration, and since vegetation is dormant, nitrogen available from animal wastes would not be utilized by plants, effectively increasing the amount of available nitrogen. Thus, water samples taken during low-flow periods in summer months may not accurately reflect spring water quality during high-discharge periods in the winter.

Based on the spring's relatively constant nitrogen content from Day 47 (January 1) to Day 94 (February 17) and the return of dissolved oxygen to normal levels, Day 47 (January 1) is considered the last day Maramec Spring was affected by the spill. The background nitrogen value used in calculating the amount of liquid fertilizer spilled is 1.0 mg/L; nitrogen passing through the spring after Day 47 (January 1) is assumed to be from other sources.

Daily nitrogen values were corrected for background nitrogen content (1.0 mg/L), and multiplied by the daily discharge to obtain the weight of nitrogen not attributable to background discharging from the spring. Daily nitrogen weights were summed to determine the minimum weight of nitrogen spilled from the pipeline: 38,642 kilograms (kg). The chemical composition of the liquid fertilizer was provided by Williams Pipeline Company. Calculations based on the chemical composition showed a nitrogen content of 32.02 percent by weight. The density of the liquid was found to be approximately 1.32 kg/L. The 38,642-kg value was corrected for the pipeline nitrogen content and specific gravity to obtain the minimum volume of material spilled: 24,153 gallons, or 575 barrels (9.143×10^4 L) (figure 5). After the pipeline break was discovered, an unknown amount of the pipeline material was pumped from pools along Dry Fork and irrigated on land adjacent to the creek. Some of the irrigation water was probably held in the soil horizon, but part of it probably entered the groundwater system. In addition, organic nitrogen was not measured at Maramec Spring, so daily nitrogen values used in the estimation are slightly lower than actual values. Appendix 1 shows the calculations used for determining the minimum amount of liquid fertilizer spilled.

Results of Public and Private Well Sampling

Groundwater movement in karst terrain is quite different from that through alluvial, glacial-drift, or massive sandstone aquifers. Because of relatively constant (for given region or aquifer) aquifer characteristics, transmissivity, and storativity, movement through these types of aquifers is generally more predictable than that through solution-altered carbonate rocks. Aquifer coefficients of carbonate units extensively modified by subsurface weathering will vary greatly over short distances. Carbonate units not extensively fractured or solution altered typically have low permeabilities, and groundwater movement is relatively slow. This even holds true for some areas in karst regions where the carbonate rock has not been significantly altered.

The open nature of the groundwater systems in the Dry Fork area allows pollutants to enter the groundwater system and travel long distances relatively quickly. However, because the conduit system has a much higher transmissivity than the adjacent host rock, it serves as a drain, thereby confining polluted groundwater to a rather narrow zone. Wells intersecting the conduit system could, of course, be affected by polluted groundwater.

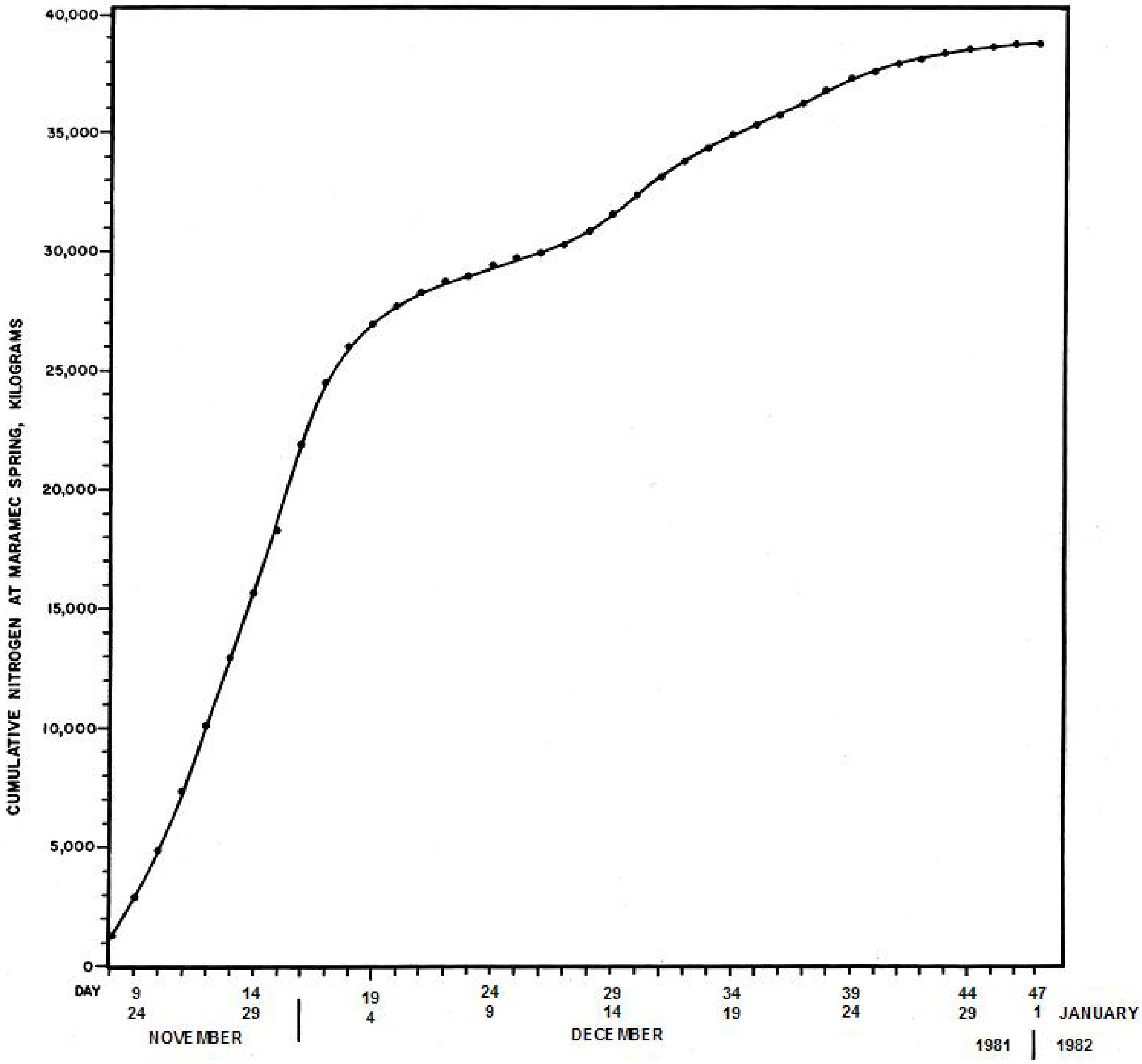

Figure 5: Cumulative nitrogen emerging from Maramec Spring; corrected for 1.0 mg/L nitrogen background.

Beginning Day 18 (December 3), Phelps County Health Department and Missouri Division of Health officials began sampling wells in a large area between the spill site and Maramec Spring. Subsequently, approximately 468 samples from 381 private wells were analyzed by the Missouri Division of Health Laboratory in Jefferson City. Table 1 and figures 6 and 7 show the results of the sampling. Approximately 50 percent of the wells sampled contained less than 1.0 mg/L nitrate; approximately 96 percent, less than 10.0 mg/L, the maximum recommended amount for human consumption. Seventeen wells contained more than 10 mg/L; 16 of them were sampled for more complete analysis to determine the source of the nitrate. The well not sampled was used for stock-watering and could only be sampled from a stock watering tank exposed to the elements. Samples were also collected from Maramec Spring and two other private wells that

Nitrate Content Range (mg/L)	Number of Wells	Percent Total Wells Sampled	Cumulative Percentage
0-0.99	190	49.87	49.87
1.0-1.99	73	19.16	69.03
2.0-2.99	29	7.61	76.64
3.0-3.99	28	7.35	83.99
4.0-4.99	8	2.10	86.09
5.0-5.99	14	3.67	89.76
6.0-6.99	7	1.84	91.60
7.0-7.99	5	1.31	92.91
8.0-8.99	3	0.79	93.70
9.0-9.99	7	1.84	95.54
10.0-10.99	5	1.31	96.85
11.0-11.99	3	0.79	97.64
12.0-12.99	0	0.00	97.64
13.0-13.99	0	0.00	97.64
14.0-14.99	4	1.05	98.69
15.0-15.99	1	0.26	98.95
16.0-16.99	0	0.00	98.95
17.0-17.99	2	0.53	99.48
18.0-18.99	0	0.00	99.48
19.0-19.99	1	0.26	99.74
20.0-20.99	0	0.00	99.74
21.0-21.99	1	0.26	100.00
Totals	381	100.0	

Table 1: Range of nitrate content of 381 private wells in the Dry Fork basin area.

contained moderate amounts of nitrate. The samples were analyzed for ammonia, nitrite, nitrate, total Kjeldahl nitrogen (TKN), orthophosphate, sulfate, and chloride. Figure 8 shows the locations of these wells and table 2 summarizes the analysis. These wells were sampled several times over a several week period. Table 3 shows variation of nitrate concentration for these wells. Ammonia values ranged from 0.01 to 0.04 mg/L, nitrite values were all less than 0.05 mg/L, and TKN ranged from less than 0.1 to 0.3 mg/L. Nitrite + nitrate values ranged from 8.1 to 20 mg/L. Sulfate content varied from less than 10 to 16 mg/L; chloride, from 10 to 34 mg/L. The wells were also sampled for bacteria and all were found to contain no coliform organisms. All public water supply wells in the spill area were sampled, and none showed increased nitrate content.

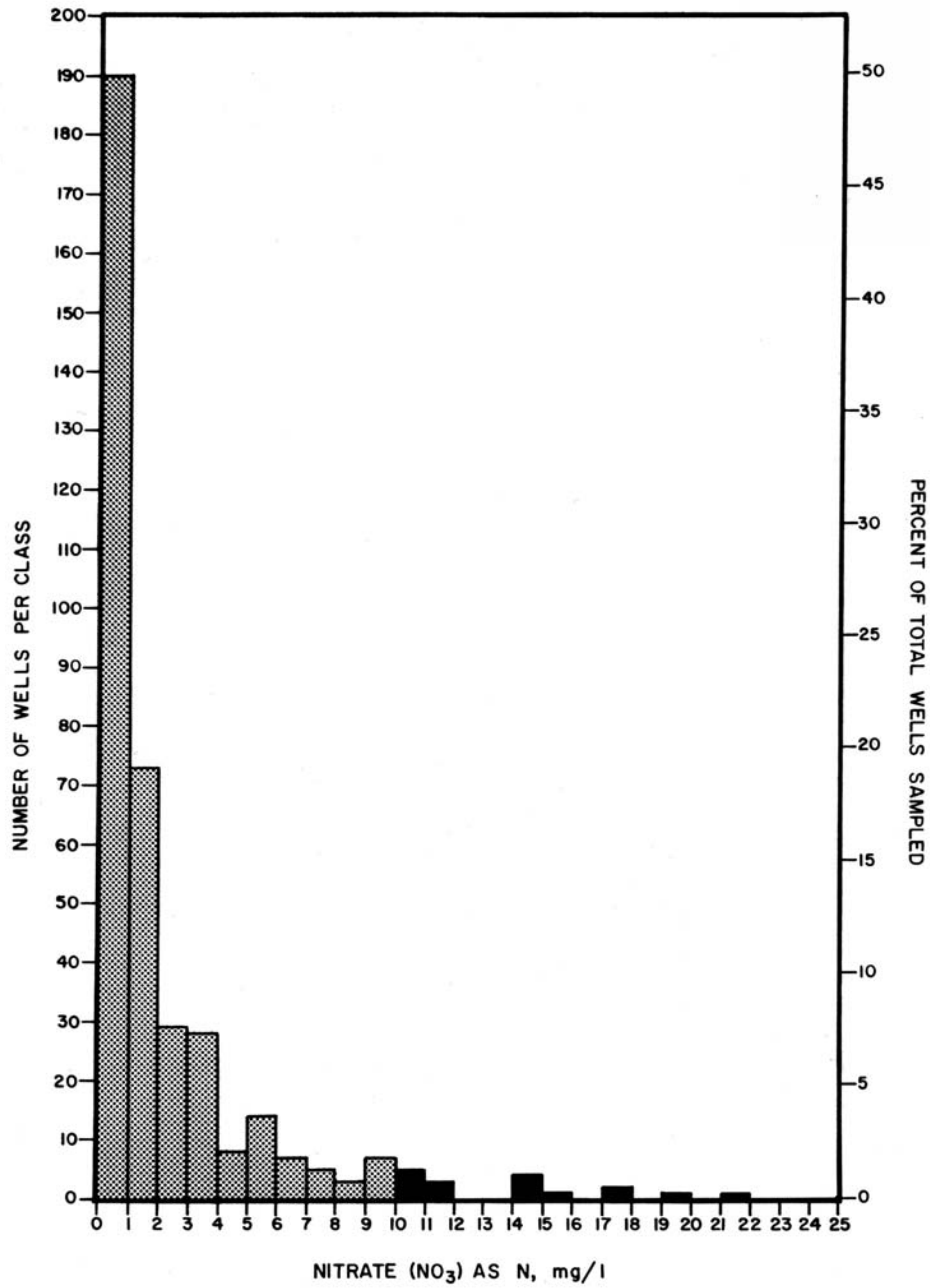

Figure 6: Number of private wells sampled versus nitrate content in the Dry Fork basin area.

Results and Conclusions

It is apparent from data presented in this report that the volume of spilled liquid fertilizer far exceeded 32 barrels (5,087 L). The 32-barrel estimate by Williams Pipeline Company was based on the size of the opening in the pipe, the pressure on the pipeline at the break site, and the estimated length of time the pipeline had been leaking. The error in estimation probably stems from the time factor; the pipeline probably began leaking several days before November 15.

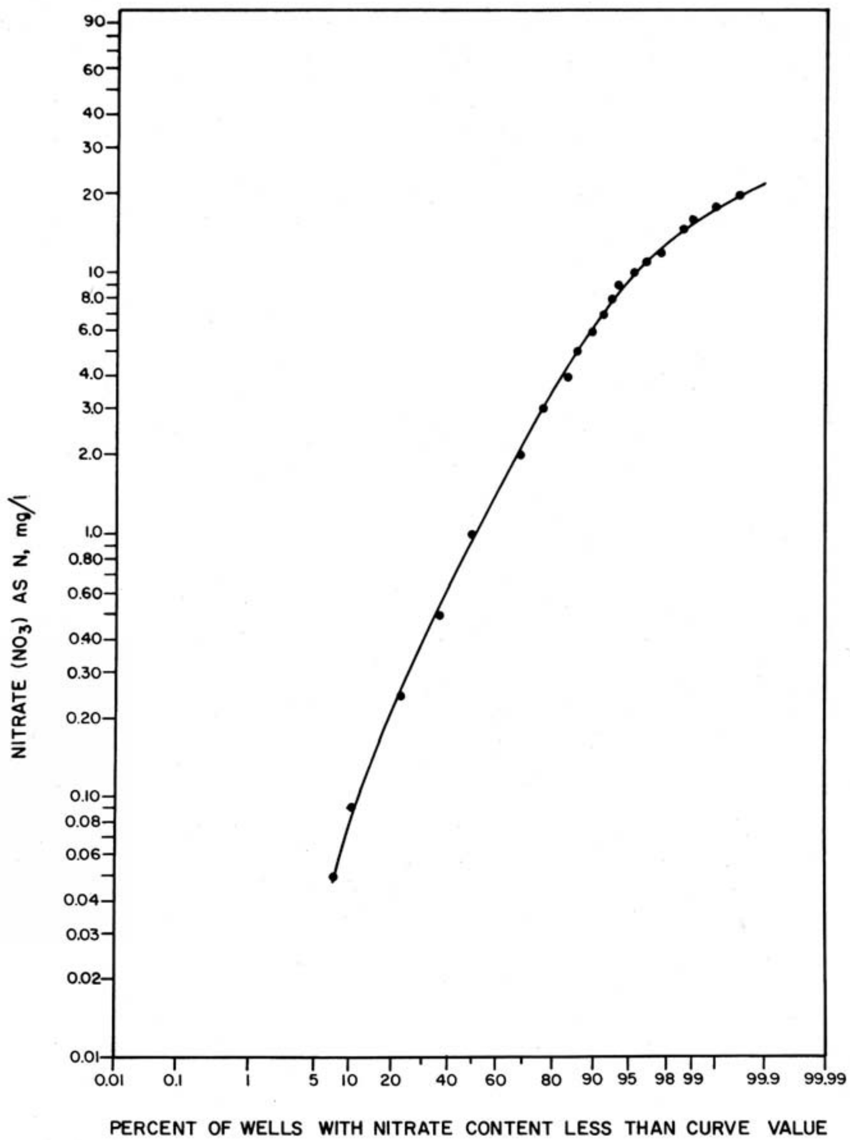

Figure 7: Cumulative frequency plot of nitrate content from 381 private wells in the Dry Fork basin area.

Water quality problems began at Maramec Spring between 5 to 7 days after the spill was reported to have occurred. Straight-line distance from the spill site to Maramec Spring is approximately 12.8 miles, requiring a minimum average velocity of between 402 ft/hr (122 m/hr) and 565 ft/hr (172 m/hr), not an impossible velocity but still quite high. Further evidence is found in the rainfall data and nitrogen graph of Maramec Spring (fig. 4). The second nitrogen peak at Maramec Spring is believed due to the large volume of nitrogen-rich water in pools downstream from the break site. Cross-section measurements along the affected reach of Dry Fork indicated the pools contained about 1.5 million gallons (5.68×10^6 L) of water when the break was reported. On Day 15 (November 30) approximately 0.75 million gallons (2.84×10^6 L) of water containing as much as 130 mg/L ammonia and 44 mg/L nitrite + nitrate remained in

the pools, the rest having been irrigated over the floodplain. Rain on Days 15 and 16 (November 30 – December 1) washed the material remaining in the pools downstream to other losing zones, where the contaminated water entered the groundwater system. The second nitrogen peak and drop in dissolved oxygen at Maramec Spring occurred about 12 days later, indicating a significantly longer travel time than the 5 to 7 days considered previously. The leak probably began at least 6 days before it was discovered, perhaps even longer, since discharge was decreasing at Maramec Spring when the break occurred, and groundwater movement was probably slower than after the November 30 – December 1 rain.

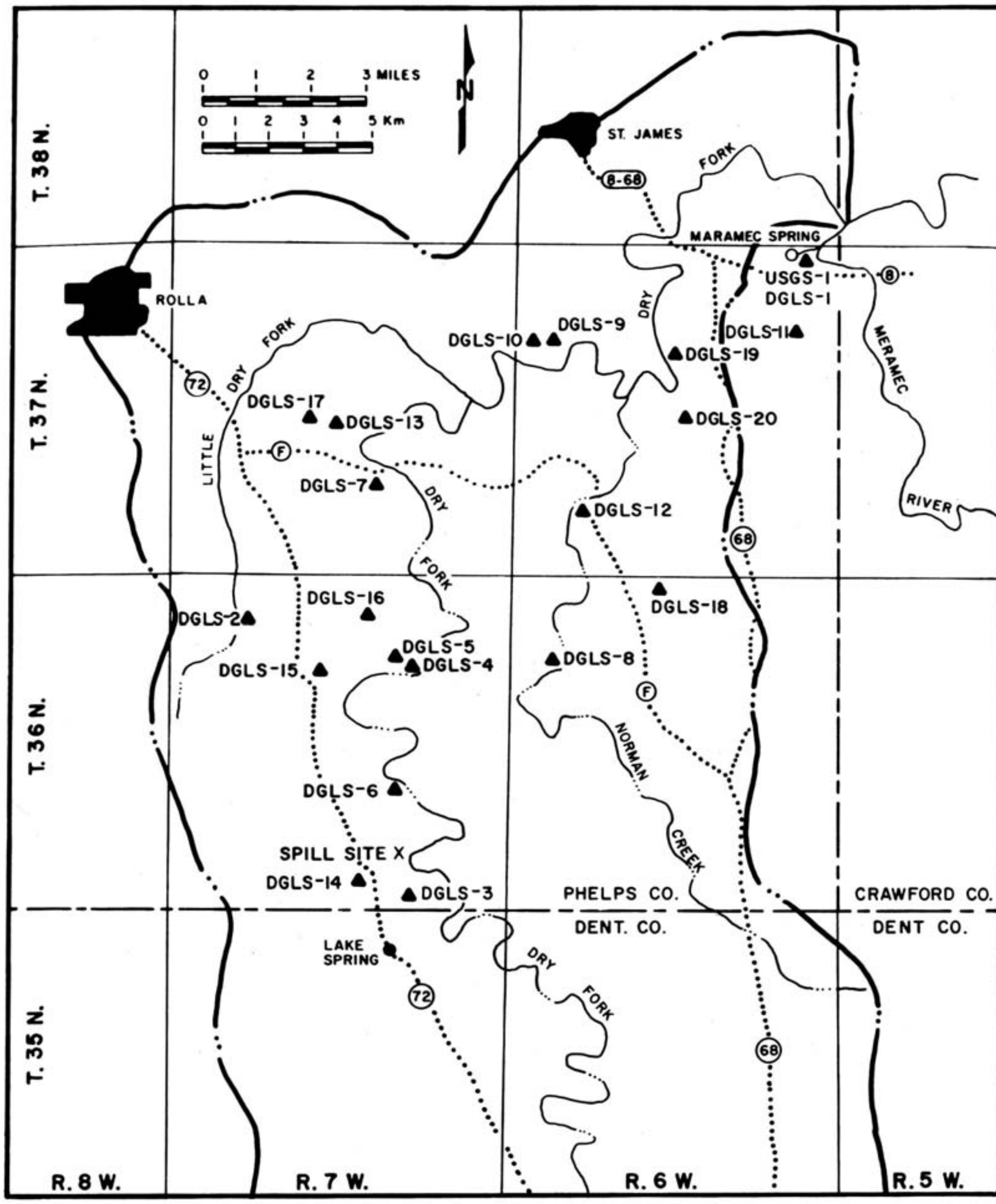

Figure 8: Location of wells with moderate and high-nitrate content in the Dry Fork basin area.

Sample Number	Sample Date	Ammonia (NH_3)mg/L	TKN Mg/L	Nitrite (NO_2) mg/L	Nitrite+Nitrate (NO_2+NO_3) mg/L	Organic Nitrogen (TKN-NH_3) mg/L	Total nitrogen mg/L	Orthopho-sphate (O-PO_4) mg/L	Sulfate (SO_4) mg/L	Chloride (Cl) mg/L
USGS-1 *	11/30/81	2.3	3.1	0.24	4.2	0.8	7.3	---	2	2.5
DGLS-1	12/14/81	0.01	0.2	<0.05	2.5	0.19	2.7	<0.05	<10	3
DGLS-2	12/14/81	0.03	0.1	<0.05	4.2	0.07	4.23	<0.05	50	40
DGLS-3	12/14/81	0.02	0.4	<0.05	3.9	0.38	4.3	<0.05	<10	10
DGLS-4	12/14/81	0.02	0.3	<0.05	15.0	0.28	15.3	<0.05	10	16
DGLS-5	12/14/81	0.04	0.2	<0.05	8.1	0.16	8.3	<0.05	<10	14
DGLS-6	12/14/81	0.03	0.1	<0.05	13.0	<0.07	13.03	<0.05	<10	20
DGLS-7	12/14/81	0.02	0.2	<0.05	12.0	0.18	12.2	<0.05	<10	15
DGLS-8	12/14/81	0.03	0.2	<0.05	17.0	0.17	17.2	<0.05	<10	10
DGLS-9	12/15/81	0.03	0.1	<0.05	15.0	0.07	15.1	<0.05	10	34
DGLS-10	12/15/81	0.01	0.2	<0.05	20.0	0.19	20.2	<0.05	<10	28
DGLS-11	12/15/81	0.02	0.2	<0.05	11.0	0.18	11.2	<0.05	<10	10
DGLS-12	12/15/81	0.01	0.1	<0.05	13.0	0.09	13.1	<0.05	<10	21
DGLS-13	1/7/82	0.02	0.2	<0.05	9.1	0.18	9.3	<0.05	<10	18
DGLS-14	1/7/82	0.02	<0.1	<0.05	11.0	<0.08	11.02	<0.05	<10	22
DGLS-15	1/7/82	0.02	<0.1	<0.05	14.0	<0.08	14.02	<0.05	<10	10
DGLS-16	1/7/82	0.02	<0.1	<0.05	10.0	<0.08	10.02	<0.05	<10	32
DGLS-17	1/7/82	0.02	0.2	<0.05	3.7	0.18	3.9	<0.05	14	9
DGLS-18	1/7/82	0.02	<0.1	<0.05	18.0	<0.08	18.02	<0.05	<10	16
DGLS-19	1/7/82	0.01	<0.1	<0.05	9.0	<0.09	9.01	<0.05	16	21
DGLS-20	1/7/82	0.03	<0.1	<0.05	13.0	<0.07	13.03	<0.05	<10	11

*Sample collected and analyzed by U.S. Geological Survey
All other samples collected by Missouri Division of Geology and Land Survey and analyzed by Missouri Division of Environmental Quality Laboratory. Samples USGS-1 and DGLS-1 from Maramec Spring. All other samples from private wells.

Table 2: Water quality analyses of Maramec Spring and high-nitrate wells in Dry Fork basin area.

DGLS-2	(12/9/81) 5.9	(12/14/81) 4.2	(12/15/81)* 4.08					
DGLS-3	(12/3/81) 3.18	(12/14/81) 3.9	(12/15/81)* 3.84					
DGLS-4	(12/10/81) 14	(12/14/81) 15	(12/15/81)* 15	(12/21/81) 20	(12/29/81) 19	(01/05/82) 24		
DGLS-5	(12/4/81) 9.1	(12/07/81) 10.4	(12/09/81) 8	(12/14/81) 8.1	(12/15/81)* 8	(12/21/81) 8	(12/29/81) 12	(01/05/82) 13
DGLS-6	(12/4/81) 16.8	(12/09/81) 12	(12/14/81) 13	(12/15/81)* 13	(12/31/81) 19			
DGLS-7	(12/4/81) 12.6	(12/09/81) 10	(12/14/81) 12					
DGLS-8	(12/8/81) 19	(12/10/81) 15	(12/14/81) 17					
DGLS-9	(12/4/81) 20	(12/08/81) 13.6	(12/15/81)* 12	(12/15/81) 15				
DGLS-10	(12/7/81) 23.4	(12/15/81)* 20	(12/15/81) 20					
DGLS-11	(12/7/81) 11	(12/14/81) 11						
DGLS-12	(12/4/81) 8.4	(12/08/81) 14.3	(12/09/81) 14	(12/15/81) 13	(12/18/81) 15	(12/29/81) 17	(01/05/82) 19	
DGLS-13	(12/9/81) 3.9	(12/10/81) 3.81	(01/07/82) 9.1					
DGLS-14	(12/9/81)* 10.8	(01/07/82) 11						
DGLS-15	(12/15/81)* 14	(12/23/81) 19	(01/07/82) 14					
DGLS-16	(12/16/81) 10	(01/07/82) 10						
DGLS-17	(1/7/82) 3.7							
DGLS-18	(12/9/81) 18.5	(12/30/81)* 23	(01/07/82) 18					
DGLS-19	(12/15/81)* 10	(01/05/82) 10	(01/07/82) 9					
DGLS-20	(12/4/81) 7.2	(12/09/81) 11	(01/07/82) 13					

(xx-xx-xx) – Date of Collection
xxx mg/L – Nitrate Concentration
*Date of analysis. Date of collection not recorded.

Table 3: Nitrate concentration changes in 19 private wells in the Dry Fork basin area.

No data indicate private wells were affected by the spill. Less than 4 percent of the wells sampled contained nitrate in excess of 10 mg/L. Periodic samples from the wells with high nitrate levels over a period of several weeks, and the ammonia, TKN, and nitrite data, indicate that the pipeline break did not cause the nitrate problem in the wells. Sulfate concentrations of three wells were above the estimated background of 5 mg/L. Chloride values ranged from 3 to 13 times the expected background value of about 3 mg/L. High nitrate and chloride contents are associated with organic waste. The data indicate that the well contamination is from some source other than the pipeline. Possible sources include nitrogen-bearing fertilizer (which is not likely, because of the time of year and the chloride content of the well water) or human waste

from septic tanks or private lagoons and animal waste. Several of these wells contained less than 30 feet of casing, which is inadequate for the area. Probably none of the wells were effectively sealed with cement grout or bentonite, and several are quite close to livestock confinements or septic systems.

Background nitrate content in the shallow aquifer in Dry Fork basin is estimated to be about 0.05 mg/L. However, due to the inherent openness of the solution-altered carbonate bedrock, improper well construction, and abundant nitrogen sources, private wells in the basin typically contain 10 to 100 times this amount. This generally true for most of the Ozark region. Analysis of public water-supply wells in the area, which generally produce from formations below the Gasconade Dolomite and contain pressure-grouted casing, showed none were affected by the pipeline break.

Although data indicate no private wells were affected by the spill, it is possible some were. The pipeline was reported to be leaking November 15, but it could have been leaking as early as November 10 or even earlier. The effects of the spill reached Maramec Spring November 22. Health authorities did not begin sampling private wells until Day 18 (December 3). By this time, nitrate content was decreasing at Maramec Spring. It is possible, though not probable, that some wells were affected by the spill before Day 18 (December 3), though the effects were undetected, much of the polluted water having already been purged from groundwater system before sampling. The groundwater system in Dry Fork basin readily accepts, transmits, and discharges enormous quantities of water; therefore, contaminants from such a break might be expected to affect a given well for only a relatively short period.

There has never been a detailed hydrogeologic study in the Dry Fork-Maramec Spring area*. During the few weeks after the pipeline break, more information was obtained about groundwater quality, surface-subsurface relationships, and direction and rate of groundwater movement than had been known before the spill. Had detailed hydrogeologic information been available, and had there been a more accurate initial estimate of the amount of pipeline material lost, much time and money would have been saved. The several days before polluted groundwater reached Maramec Spring could have been used to collect background data and relocate the trout at Maramec Spring. Health authorities would have been better able to assess the possible impact on private water supplies, and background water-quality sampling of private water supplies could have begun immediately after the spill. Detailed hydrogeologic studies are expensive but must be viewed as an investment. In karst terrain it is seldom possible to confine a large spill and remove the material before it enters the groundwater system; after a spill, only nature can be counted on to clean it up. In many cases, a hydrologic model constructed from detailed surface-water and groundwater information can be applied in several areas sharing similar hydrologic and geologic characteristics. Pipelines are necessary for fluid transport, but there will be pipeline breaks no matter how well lines are monitored and maintained. Accurate, detailed information about surface-water and groundwater must be available so that intelligent decisions can be made quickly in the event of spills.

*(a more detailed study of the Maramec Spring system was published in 1996 and can be found using the following link: http://www.dnr.mo.gov/env/wrc/docs/WR55.pdf)

ADDENDUM: WILLIAMS PIPELINE LEAK – MARAMEC SPRING WATER TRACE

On May 13, 1982, three gallons of Rhodamine WT (20%) fluorescent dye was introduced into the unnamed spring-fed tributary of Dry Fork where the pipeline leak occurred in the NE ¼ Sec. 35, T. 36 N., R. 7 W. (photo 5). The dye was carried downstream into Dry Fork, a few hundred feet to the east. For the next mile downstream, Dry Fork consisted of several pools connected by flow. Downstream from the pools there was no flow for the next several miles. The dye reappeared at Maramec Spring, 12.8 miles to the northeast, between 11 and 12 days after in was injected. The dye was detected in both activated charcoal packets and in water samples collected from the spring (figure 9). The straight-line velocity of the dye through the groundwater system was between 1.07 and 1.16 miles per day.

Photo 5. Rhodamine WT fluorescent dye being injected at the spill site.

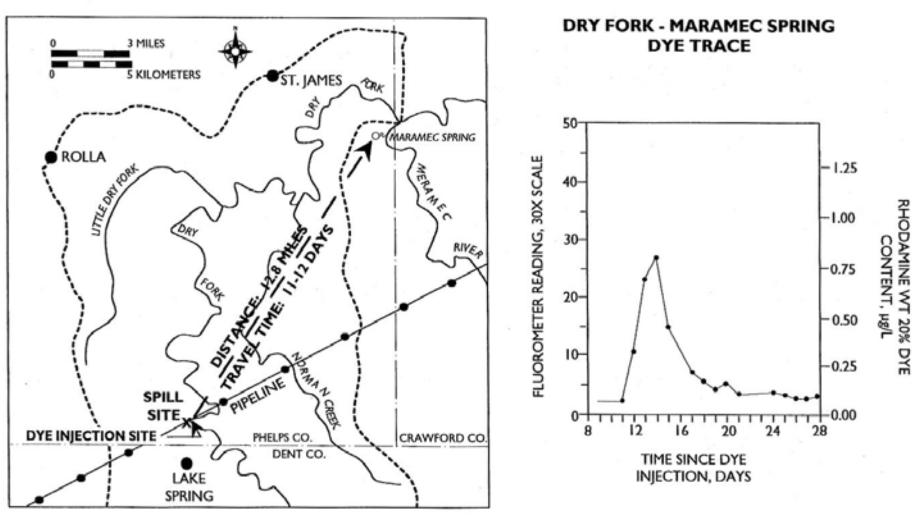

Figure 9. Results of the Williams Pipeline Leak-Maramec Spring water trace.

References Cited

Gann, E.E. and Harvey, E. J., 1975, Norman Creek, a source of recharge to Maramec Spring, Phelps County: U.S. Geological Survey Journal of Research, v. 3, no. 1, p. 99-102.

Vineyard, Jerry D. and Gerald L. Feder, 1974, Springs of Missouri: Missouri Geological Survey and Water Resources, Water Resources Report No. 29, p. 155-157.

Appendix 1

Calculations used in determining the minimum amount of liquid fertilizer spilled

Converting discharge data from cubic feet per second (ft^3/sec) to liters per day (L/day):

$$1\ ft^3/sec \times (2.832 \times 10^{-2}\ \frac{m^3/sec}{ft^3/sec}) \times 1000\ L/m^3) = 28.32\ L/sec$$

$$28.32\ L/sec \times 60\ sec/min \times 60\ min/hr \times 24\ hr/day = 2.447 \times 10^6\ L/day$$

Calculating percent nitrogen in the liquid fertilizer:

(Analyses of ammonium nitrate – urea – water provided by Williams Pipeline Company)

45.1 % NH_4NO_3 (ammonium nitrate)
34.8 % H_2NCONH_2 (urea)
<u>20.1 %</u> H_2O (water)
100.0 %   (also a corrosion inhibitor, Corblok, 100 mg/L, and fluorescent dye,1 mg/L)

atomic weights

N – 14.0067
H – 1.00797
O – 15.9994
C – 12.0115

NH_4NO_3

(14.0067)2 + (1.00797)4 + (15.9994)3 = 80.04348

NH_4NO_3 = 80.0438   2N = 28.0134

H_2NCONH_2

(14.0067)2 + (1.00797)4 + 15.9994 + 12.0115 = 60.05618

H_2NCONH_2 = 60.05618   2N = 28.0134

(28.0134/80.04348 x 0.451) + (28.0134/60.05618 x 0.348) = 0.320165 or 32.02 % nitrogen

Nitrogen content of the liquid fertilizer = 32.02 percent

Month	Day	Maramec Spring Discharge, liters/day	Nitrogen Content (NO_2+NO_3+NH_3), Mg/L (corrected for 1 mg/L background)	Daily Nitrogen, kg	Cumulative Nitrogen, kg
Nov	23	5.6278×10^8	2.39	1345.0	1345.0
Nov	24	5.5543×10^8	2.80	1555.2	2900.2
Nov	25	5.5543×10^8	3.53	1960.7	4860.9
Nov	26	5.5299×10^8	4.50	2488.5	7349.4
Nov	27	5.4565×10^8	5.08	2771.9	10121.3
Nov	28	5.4565×10^8	5.14	2804.6	12925.9
Nov	29	5.5299×10^8	4.94	2731.8	15657.7
Nov	30	5.7746×10^8	4.52	2610.1	18267.8
Dec	1	1.10353×10^9	3.32	3663.7	21931.5
Dec	2	1.09619×10^9	2.37	2598.0	24529.5
Dec	3	1.02034×10^9	1.52	1550.9	26080.4
Dec	4	8.5640×10^8	1.03	882.1	26962.5
Dec	5	7.6342×10^8	0.96	732.9	27695.4
Dec	6	7.1693×10^8	0.84	602.2	28297.6
Dec	7	6.9001×10^8	0.65	448.5	28746.1
Dec	8	6.3863×10^8	0.54	344.9	29091.0
Dec	9	6.0682×10^8	0.54	327.7	29418.7
Dec	10	5.8724×10^8	0.45	264.3	29683.0
Dec	11	5.7990×10^8	0.40	232.0	29915.0
Dec	12	5.7746×10^8	0.57	329.2	30244.2
Dec	13	5.6767×10^8	1.00	567.7	30811.9
Dec	14	5.6033×10^8	1.32	739.6	31551.5
Dec	15	5.5543×10^8	1.50	833.1	32384.6
Dec	16	5.5299×10^8	1.37	757.6	33142.2
Dec	17	5.3341×10^8	1.23	656.1	33798.3
Dec	18	5.3097×10^8	1.05	557.5	34355.8
Dec	19	5.0894×10^8	0.96	488.6	34844.4
Dec	20	5.0405×10^8	0.96	483.9	35328.3
Dec	21	5.1384×10^8	0.87	447.0	35775.3
Dec	22	5.4075×10^8	0.78	421.8	36197.1
Dec	23	8.9065×10^8	0.67	596.7	36793.8
Dec	24	9.3714×10^8	0.48	449.8	37243.6
Dec	25	8.6374×10^8	0.38	328.2	37571.8
Dec	26	8.0746×10^8	0.34	274.5	37846.3
Dec	27	7.6831×10^8	0.29	222.8	38069.1
Dec	28	6.9735×10^8	0.28	195.3	38264.4
Dec	29	6.4841×10^8	0.25	162.1	38426.5
Dec	30	5.8724×10^8	0.22	129.2	38555.7
Dec	31	5.7990×10^8	0.14	81.2	38636.9
Jan	1	5.5788×10^8	0.01	5.6	38642.5
Total		2.6392×10^{10}		38642.5	

Volume of water discharging from Maramec Spring from November 23, 1981 through January 1, 1982 = 2.6392×10^{10} Liters

Amount of nitrogen passing through Maramec Spring November 23, 1981 through January 1, 1982 = 38642.5 kg or 3.86425×10^{10} mg

Average nitrogen content, Maramec Spring, November 23, 1981 through January 1, 1982 =

$$\frac{3.86425 \times 10^{10}\ \text{mg}}{2.6392 \times 10^{10}\ \text{L}} = 1.46\ \text{mg/L}$$

Calculation of the volume of pipeline fluid passing through Maramec Spring:

Nitrogen content of pipeline fluid = 32.02 percent
Measured specific gravity of pipeline fluid = 1.32 kg/L

$$\frac{3.86425 \times 10^{4}\ \text{kg}}{0.3202} \times \frac{1\ \text{L}}{1.32\ \text{kg}} = 9.1426 \times 10^{4}\ \text{L}$$

$$9.1426 \times 10^{4}\ \text{L} \times \frac{1\ \text{gallon}}{3.78531\ \text{L}} = 2.4153 \times 10^{4}\ \text{gallons}$$

$$\frac{2.4153 \times 10^{4}\ \text{gallons}}{42\ \text{gallons/barrel}} = 575\ \text{barrels}$$

Estimate of the minimum amount of pipeline fluid spilled: 24,153 gallons of 575 barrels